Preparation and Characterization of Novel Aromatic-inserted Tris-fused Tetrathiafulvalenes

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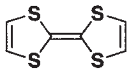
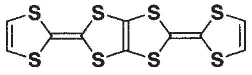
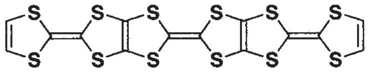
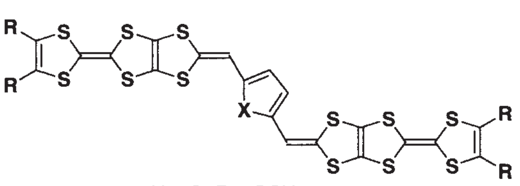
New families of extended tris-fused TTFs, in which aromatic rings are inserted, have been synthesized. Cyclic voltammetry and theoretical calculation of them indicate electronic structure of the furan and thiophene derivatives may be regarded as tris-fused TTFs, whereas the benzene derivative as a dimeric (2-methylidene-1,3-dithiolo[4,5-*d*])-TTF.

Recently we have reported a number of stable metallic salts based on the cation radical salts of 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP) derivatives,[1] into which two tetrathiafulvalenes (TTF) directly fuse with each other. Such an unusual conducting property is due to two-dimensional intermolecular interactions derived from both extension of π-conjugation and ladder arrangement of multi-sulfur atoms. In this context, tris-fused TTF derivatives have aroused much interest because of much larger π-system and more sulfur atoms. As further investigation, such nano-size extended TTF molecules are also expected to be promising multi-redox components toward novel electronic materials.[2] However, a few tris-fused TTF (BDT-TTPY) derivatives[3] are known because of their low solubility. Thus, it is necessary to develop a novel tris-fused TTF system. We have focused on an aromatic-inserted tris-fused TTF skeleton, because the flexibility of single bonds connected to an inserted aromatic ring is expected to enhance solubility. In this letter, we describe preparation and physicochemical property of novel tris-fused TTF derivatives **1–3**, and conducting properties of their charge transfer complexes.


TTF

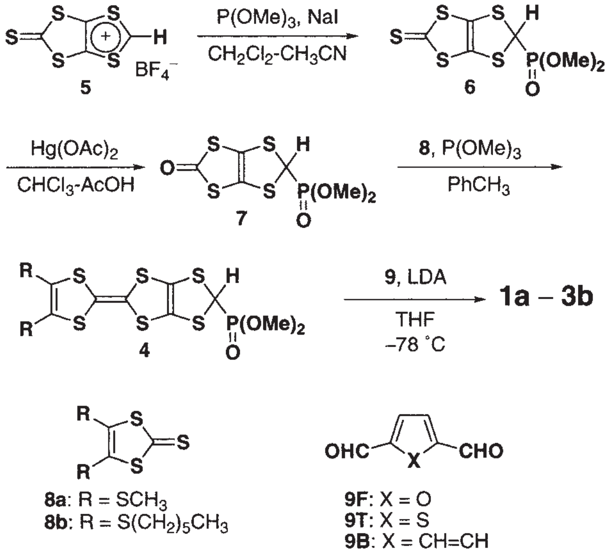

BDT-TTP


BDT-TTPY



1a: X = O, R = SCH_3,
1b: X = O, R = $S(CH_2)_5CH_3$
2a: X = S, R = SCH_3
2b: X = S, R = $S(CH_2)_5CH_3$
3a: X = CH=CH, R = SCH_3
3b: X = CH=CH, R = $S(CH_2)_5CH_3$

MDT-TTF phosphonate esters **4** are key intermediates to target aromatic-inserted tris-fused TTF derivatives, because the Wittig-Horner type reaction generally gives the desired product in a high yield compared with phosphite-mediated cross-coupling. We used a 1,3-dithiolium salt **5**[4] as a starting compound. It was easily converted to phosphonate methyl ester **6** by the reaction with trimethylphosphite in the presence of sodium iodide (82%). Treatment with mercury(II) acetate in $CHCl_3$-acetic acid gave corresponding ketone **7** as a colorless stable solid (86%). The cross-coupling reaction of the ketone **7** with 4,5-bis(alkylthio)-1,3-dithiol-2-thiones **8** afforded MDT-TTF phosphonate esters **4** in 27–45% yields. The Wittig–Horner reaction was carried out by adding 2.5 equiv. BuLi in hexane to the mixture of dicarboxaldehyde **9** and **4** in THF at −78 °C to give **1–3** in 53–75% yields.[5]



Scheme 1.

Unfortunately, any single crystal suitable for an X-ray analysis has never been obtained. In order to acquire the information on their molecular structures, we have optimized molecular structures of the unsubstituted **1** and **3** using RHF/6-31G* method.[6] Their optimized structures are shown in Figure 1.

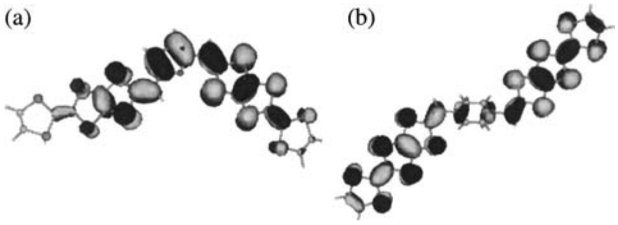


Figure 1. Optimized molecular geometries and HOMO of (a) unsubstituted furan derivative **1** and (b) unsubstituted benzene derivative **3**.

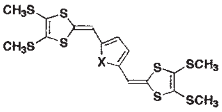
There are two remarkable differences between these two molecules. Firstly, the dihedral angles between a central aromatic ring and neighboring 1,3-dithiole rings is large value of 40.1° in the benzene derivative **3**, while **1** has relatively high planarity of those of 2.3 and 17.9°, respectively. These results are also supported by the observation of longer absorption maximum of **1b** compared with **3b**.[5] Probably this is due to a steric hindrance between *peri* hydrogen atoms on the benzene ring and 1,3-dithiole rings. Secondly, HOMO of the furan derivative is mainly localized on the central π-extended TTF part, whereas that of the benzene derivative is placed on the both DT-TTF units. This suggests that the different parts mainly contribute to the first oxidation process.

Redox potentials of tris-fused TTFs **1b–3b** measured by cyclic voltammetry are summarized in Table 1.[7] The furan and thiophene derivatives **1b** and **2b** showed two one-electron oxidation waves and successively two two-electron oxidation waves, whereas the benzene derivative **3b** demonstrated only three-pairs of two-electron oxidation waves. The E_2–E_1 values of **1b** and **2b** are comparable to those of **10** and **11**, indicating that two positive charges in $\mathbf{1b}^{2+}$ and $\mathbf{2b}^{2+}$ mainly distribute on the central extended-TTF moiety as is often observed in extended-TTP donors.[8] Furthermore, the voltammograms of phenyl substituted DT-TTF **13** showed a quite similar behavior to the benzene derivative **3b**. The order of the first redox potentials (**1b** < **2b** < **3b**) is consistent with that of aromaticity in the central aromatic rings. The above results strongly indicate two positive charges in $\mathbf{3b}^{2+}$ are located on the outer TTF units so as both to preserve aromaticity of the central benzene ring and to avoid steric hindrance between *peri* hydrogen atoms on the benzene ring and 1,3-dithiole rings as a result of formation of a planar quinoid structure. Therefore, it could be concluded that the benzene derivative **3** should be regarded as a DT-TTF dimer rather than a tris-fused TTF system.

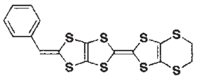
Table 1. Redox Potentials of **1b–3b** and Their Related Donors (vs Ag/Ag$^+$, Pt electrode, 0.1M Bu_4NPF_6 in benzonitrile)

Donor	E_1	E_2	E_3	E_4	E_5	E_6
1b	0.00	0.12	0.45(2e)		0.71(2e)	
2b	0.06	0.19	0.46(2e)		0.74(2e)	
3b	0.17(2e)		0.45(2e)		0.86(2e)	
10	-0.04	0.09				
11	0.06	0.14				
12	0.27[a]	0.47[a]				
13	0.15	0.50	0.93			

[a] Irreversible waves. Anodic peak potentials.



10: X = O
11: X = S
12: X = CH=CH



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Conducting charge transfer complexes were obtained by the reaction of each donor with $TCNQF_4$ or DDQ in chlorobenzene solution. The electrical conductivity and composition are shown in Table 2. In spite of no stripe-like structure like BDT-TTP, most complexes show relatively high conductivity of $\sigma_{rt} = 10^{-1}$–$10^{0}\,S\,cm^{-1}$ on a compressed pellet. This indicates that the conductivities of the tris-fused TTFs can be enhanced by the extended π-conjugation.

Table 2. Electrical Conductivities of Charge-Transfer Complexes of **1a–3a**

Donor	Acceptor	D : A	$\sigma_{rt}/S\,cm^{-1}$	E_a/eV
1a	$TCNQF_4$	1 : 1	0.30	0.059
	DDQ	2 : 3	0.10	0.082
2a	$TCNQF_4$	1 : 1	2.2	0.034
	DDQ	4 : 7	0.42	0.068
3a	$TCNQF_4$	2 : 3	9.0	0.033
	DDQ	2 : 3	4.6×10^{-3}	0.131

Further investigation on development of much larger molecules based on multi-TTF systems is currently in progress.

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5 All spectral data are consistent with the molecular structure of each compound. Selected compound data are as follows; **1b**: ^1H NMR (400 MHz, CS_2–C_6D_6) δ 6.29 (s, 2H), 6.11 (s, 2H), 2.72 (t, 8H), 1.28–1.60 (m, 32H), 0.89 (m, 12H); Mass m/z 1111 $[M–H]^+$; UV-vis (CH_2Cl_2) λ_{max} 453.5, 431.5, 312.0 nm; **2b**; ^1H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2H), 6.55 (s, 2H), 2.72 (t, 8H), 1.28–1.59 (m, 32H), 0.87 (m, 12H); Mass m/z 1127 $[M–H]^+$; UV-vis (CH_2Cl_2) λ_{max} 470.5, 446.0(sh), 315.0 nm; **3b**; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 4H), 6.39 (s, 2H), 2.72 (t, 8H), 1.25–1.56 (m, 32H), 0.89 (m, 12H); Mass m/z 1121 $[M–H]^+$; UV-vis (CH_2Cl_2) λ_{max} 439.5, 418.0(sh), 339.0 nm.

6 The molecular orbital calculation was carried out using the Gaussian 98 program. M. J. Frish et al., Gaussian 98, Gaussian, Inc., Pittsburgh, PA (1998).

7 All the new tris-fused TTFs are more soluble than the corresponding BDT-TTPY derivatives. For example, cyclic voltammetry of **1b–3b** can be achieved in benzonitrile, whereas the addition of CS_2 is needed to obtain satisfactory voltammogram of tetrakis(hexylthio)-BDT-TTPY.

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